*The Decomposition of αα'-Azo*iso*butyronitrile in Solution.*

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The decomposition of αα'-azo*iso*butyronitrile in dilute solutions has been studied by estimating the tetramethylsuccinodinitrile and *iso*butyronitrile formed by combination and disproportionation respectively of the 2-cyano-2-propyl (1-cyano-1-methylethyl) radicals produced from the azo-compound. Dilute solutions of the azo-compound, labelled with ^{14}C, have been used, their concentrations being similar to those when the compound is used as an initiator of polymerizations. The products have been estimated by the method of isotopic dilution. In the early stages of the decomposition, disproportionation occurs more frequently than combination, but as decomposition proceeds combination becomes predominant.

Bevington, Bradbury, and Burnett (*J. Polymer Sci.*, 1954, **12**, 469) described a new method for determination of the rates of initiation in radical polymerizations; it involved the use of an initiator which can be estimated with accuracy in very small concentrations so that the exact amount of initiator combined in the polymer can be determined. This requirement is met if the initiator is labelled with a radioactive isotope; the initiator most frequently used has been αα'-azo*iso*butyronitrile (referred to as AZDN in Tables of results) labelled with ^{14}C on the methyl groups. If the rate of decomposition of the initiator is known, it is possible to calculate the efficiency with which radicals formed from it initiate polymerization. It has been found that for a number of systems this efficiency is well below 100%, frequently being near 50%; a number of American workers (see, *e.g.*, Arnett and Peterson, *J. Amer. Chem. Soc.*, 1952, **74**, 2031) have concluded that in many cases the efficiency is close to 100%.

A way to decide between these conflicting views on initiator efficiency would be to detect and estimate products formed from those radicals which do not initiate polymerization. Analysis by conventional methods is impracticable because of the small weights of the substances involved and the complexity of the mixture. The analysis can be performed satisfactorily by using a labelled initiator and the method of isotopic dilution.

The most thorough study of the products resulting from the decomposition of αα'-azo*iso*butyronitrile is that of Bickel and Waters (*Rec. Trav. chim.*, 1950, **69**, 1490). Their work suggests that almost all the wasted 2-cyano-2-propyl radicals would combine to give tetramethylsuccinodinitrile (referred to as TMSDN in Tables of results). It has been found that during the polymerization of styrene at 60° initiated by the thermal decomposition of αα'-azo*iso*butyronitrile, the dinitrile is indeed formed but it is accompanied by an appreciable quantity of *iso*butyronitrile (referred to as IBN in the Tables); this substance is probably formed by the disproportionation of pairs of the radicals. If allowance is made for both combination and disproportionation of wasted radicals, it is confirmed that the efficiency is well below 100%. In view of the difference between the nature of the products from the interaction of the radicals in these experiments and in those of Bickel and Waters (*loc. cit.*), a study of the decomposition of αα'-azo*iso*butyronitrile in inert solvents was undertaken.

Experiments were conducted in benzene, toluene, and carbon tetrachloride under conditions similar to those used in the experiments with styrene. Other experiments were performed under the conditions used by Bickel and Waters (*loc. cit.*); further experiments were carried out in an attempt to correlate the two sets of results.

EXPERIMENTAL

Materials.—αα'-Azo*iso*butyronitrile labelled with ^{14}C was prepared in connection with previous work (Bevington, Melville, and Taylor, *J. Polymer Sci.*, 1954, **12**, 449). Solvents were dried and redistilled before use. Inactive tetramethylsuccinodinitrile was prepared (Bickel and Waters, *loc. cit.*) and recrystallized from ethanol. Inactive *iso*butyronitrile was made by dehydration of *iso*butyramide and purified by distillation.

Reaction Mixtures.—A weighed amount of the labelled azo-compound and a known volume of solvent were introduced into the reaction vessel. When necessary the solution was degassed on the vacuum line and the vessel was sealed.

Isolation of Products.—The reaction mixture was mixed with known weights of inactive tetramethylsuccinodinitrile and *iso*butyronitrile dissolved in ethanol. The solution was separated into a liquid and a solid portion by distillation at low temperatures on the vacuum line. From the solid consisting of tetramethylsuccinodinitrile and a much smaller weight of undecomposed azo-compound, pure dinitrile was recovered by repeated recrystallization from ethanol. The liquid was redistilled and then the *iso*butyronitrile contained in it was converted into the amide through the acid and the acid chloride. The amide was recrystallized from benzene.

Assay Procedure.—The specific activities of the active substances were compared by the method of gas-counting (Bevington, Melville, and Taylor, *loc. cit.*; Bevington, Guzman, and Melville, *Proc. Roy. Soc.*, 1954, *A*, **221**, 437), the carbon dioxide being obtained by wet combustion. In the experimental results, corrected counting rates in counts per minute (c/m.) for a standard filling of the counter are quoted. The counting rate is directly proportional to the $^{14}C : ^{12}C$ ratio in the material oxidized.

Calculation of Results.—The weight of product formed in the decomposition is calculated from the known weight of carrier and the counting rates of the diluted product and the original azo-compound.

Results. Tests on Purification Procedures.—It is an essential of the method that tetramethylsuccinodinitrile and *iso*butyramide of high purity should be recovered from the mixture, and tests on the efficiencies of the purifications were made. Mixtures of labelled αα′-azo*iso*butyronitrile and much larger weights of unlabelled tetramethylsuccinodinitrile were made, and the latter was recovered by recrystallization from ethanol. After each crystallization the dinitrile was assayed; any activity found in it must have been due to incomplete removal of the azo-compound, to decomposition during recrystallization, or to exchange reactions. Tests showed that after three crystallizations the amount of activity in the dinitrile was small. The results in Table 1 indicate that in experiments where tetramethylsuccinodinitrile of fairly low activity is separated from a much smaller weight of αα′-azo*iso*butyronitrile of high activity by repeated crystallization, a small correction must be made to the observed activity of the dinitrile even after three crystallizations. The magnitude of this correction appears to be small and it can be estimated from the results of these test separations.

TABLE 1.

	Test 1	Test 2	Test 3
Wt. of AZDN (96,500 c/m.) (mg.)	10·0	14·7	34·8
Wt. of inactive TMSDN (mg.)	1441	769	1257
Calc. c/m. for no separation	551	1505	2170
Obs. c/m. for TMSDN after successive crystallizations...	35, 13	64, 18·5	317, 32, 19

In an experiment in which labelled *iso*butyramide was isolated, the product was recrystallized three times and assayed after each crystallization. The counting rates at the three stages were 384, 387, and 373; the m. p. of the product was sharp after the first crystallization. These results show clearly that the procedure adopted for purification of this compound was satisfactory.

When the alcoholic solution containing active materials and carriers is separated into solid and liquid fractions, it is possible that active αα′-azo*iso*butyronitrile and tetramethylsuccinodinitrile might sublime and be mixed with the *iso*butyronitrile in the liquid fraction. The amide prepared from this nitrile is recrystallized and the test described above shows that the tetramethylsuccinodinitrile (or products derived from it) are eliminated; if αα′-azo*iso*butyronitrile is present in the *iso*butyronitrile however it would be decomposed during the hydrolysis of the nitrile and the weight of nitrile found would not be that produced in the original decomposition.

In all experiments the distillate from the vacuum-distillation was redistilled, but in one case about ½ g. of inactive tetramethylsuccinodinitrile and about ½ g. of inactive azo-compound were added to the liquid before the second distillation. If sublimation of αα′-azo*iso*butyronitrile is serious, the error in this experiment would result in a decrease in the specific activity of the recovered *iso*butyramide and therefore in an apparent decrease in the amount of active *iso*butyronitrile present in the original liquid. The conditions were chosen so that they were favourable for sublimation, the dry solid being left connected to the cold trap for about 30 min.

In this experiment it was found that 43·6% of the $CN{\cdot}CMe_2{\cdot}$ radicals apparently underwent combination, whereas in a similar experiment carried out in the normal manner, this percentage was 35. The difference was due to the fact that in the special experiment the specific activity of the amide was less than in the routine experiment. Clearly, sublimation occurs to some extent, but even in an experiment in which its effect was deliberately made much larger than usual, the effect upon the final result was not very large; for this reason sublimation is neglected in calculation of results. Any errors due to sublimation cannot affect analyses for tetramethylsuccinodinitrile, and in all cases there was agreement between the amount of azo-compound decomposed, calculated from the known rate of decomposition, and the amount calculated from the found weights of products.

Experiments at 60°.—Solutions of αα′-azo*iso*butyronitrile in benzene, toluene, and carbon tetrachloride were treated in ways similar to the solutions of initiator in styrene. The concentration of the azo-compound was in the region of 5 mg./ml., and the solutions, which were free from air, were kept at 60° for periods of 5—9 hr. so that between 15% and about 25% of the azo-compound was decomposed. These experiments are summarized in Table 2.

TABLE 2.

Expt. :	No. 1	No. 2	No. 3	No. 4	Nc. 5
Wt. of AZDN (mg.)	25·5	21·3	26·1	20·2	20·9
Vol. of solvent (ml.) †	6·0B	4·3T	4·8B	5·1T	4·0C
Time at 60° (hr.)	6·0	8·75	6·5	9·0	4·75
Calc. % of AZDN decomposed	18·5	25·9	20·0	26·5	15·0
Wt. of TMSDN (mg.) found	1·42	1·75	1·56	*	0·825
Wt. of IBN (mg.) found	1·24	*	*	1·36	0·80
AZDN equiv. of TMSDN (mg.)	1·71	2·11	1·88	*	0·99
AZDN equiv. of IBN (mg.)	2·95	*	*	3·24	1·88
% of radicals combining	36·7	38·2	36·0	39·5	34·5

* No analysis performed. † B = Benzene; T = toluene; C = carbon tetrachloride.

The velocity constant for the first-order decomposition of αα′-azo*iso*butyronitrile at 60° is taken as $9{\cdot}52 \times 10^{-6}$ sec.$^{-1}$; this value, taken from Bawn and Mellish's data (*Trans. Faraday Soc.*, 1951, **47**, 1216), is in reasonable agreement with values of other workers. It is assumed that *iso*butyronitrile results from the disproportionation of pairs of radicals; this is discussed later. Calculations of the percentages of radicals combining are based on the calculated amount of αα′-azo*iso*butyronitrile decomposed except where analyses for both tetramethylsuccinodinitrile and *iso*butyronitrile were performed; in these cases the results of the two analyses were used in the calculations.

In another series of experiments solutions of the azo-compound in benzene (about 5 mg./ml.) were degassed and kept at 60° for 2—115 hr., so that the percentage decomposed ranged from about 6% to about 98%. Results are presented in Table 3.

TABLE 3.

Expt. :	No. 6	No. 7	No. 8	No. 9	No. 10
Wt. of AZDN (mg.)	16·1	28·4	10·4	15·3	10·7
Vol. of benzene (ml.)	3·1	6·0	2·0	3·0	2·0
Time at 60° (hr.)	2·0	3·55	24·5	43·25	114·25
Calc. % AZDN decomposed	6·54	11·4	56·8	77·3	98·1
Wt. of TMSDN (mg.) found	0·195	0·60	2·36	5·73	5·97
Wt. of IBN (mg.) found	0·270	0·82	0·80	0·98	0·45
AZDN equiv. of TMSDN (mg.)	0·24	0·72	2·85	6·91	7·20
AZDN equiv. of IBN (mg.)	0·64	1·94	1·90	2·33	1·08
% of radicals combining	27·3	27·0	60·0	74·8	87·0

In order to see if the decomposition is influenced by air, a solution containing 28·4 mg. of αα′-azo*iso*butyronitrile in 6·0 ml. of toluene was kept at 60° for 3·5 hr. with free access of air (Expt. No. 11) and afterwards 0·61 mg. of tetramethylsuccinodinitrile and 0·82 mg. of *iso*butyronitrile were found in the solution, indicating that 28·0% of the radicals underwent combination. The calculated weight of αα′-azo*iso*butyronitrile decomposed is 3·25 mg., and the weight equivalent to the found tetramethylsuccinodinitrile and *iso*butyrinitrile was 2·68 mg. The results of this experiment are closely similar to those of Expt. No. 7, showing that the decomposition is hardly affected by air.

Some experiments (see Table 4) were performed at 60° in the absence of air but in the presence of either tetramethylsuccinodinitrile or *iso*butyronitrile, both of which are products of the decomposition.

Solutions of αα′-azo*iso*butyronitrile in pure styrene were degassed and kept at 60°; the polymers were recovered by precipitation in alcohol. In Expt. No. 15 tetramethylsuccinodinitrile and *iso*butyronitrile were contained in the alcohol; in Expt. No. 16 the solution of polymer in monomer was mixed with benzene containing the carriers before precipitation. Samples of pure tetramethylsuccinodinitrile and *iso*butyramide were recovered by the methods described already. The relevant features of two experiments are shown in Table 5; these and similar experiments will be discussed in another paper. It is evident that the relative importances of combination and disproportionation in the interaction of pairs of CN•CMe$_2$• radicals is about the same in styrene as in benzene, toluene, and carbon tetrachloride.

TABLE 4.

		Expt. No. 12	No. 13	No. 14
Wt. of AZDN (mg.)	In reaction mixture	26·7	20·6	16·2
Vol. of benzene (ml.)		5·0	0	4·2
Wt. of TMSDN (mg.)		553·8	0	0
Wt. of IBN (mg.)		0	3090	695
Time at 60° (hr.)		23·75	23·75	19·17
Wt. of TMSDN (mg.) found	Formed in decomposn.	6·73	3·25	2·28
Wt. of IBN (mg.) found		1·49	0·28	0·32
AZDN equiv. of TMSDN (mg.)		8·11	3·92	2·75
AZDN equiv. of IBN (mg.)		3·54	0·67	0·77
% decomposn. of AZDN by calcn.		55·7	55·7	48·1
% decomposn. of AZDN from products		43·6	22·3	22·3
% radicals combining		69·6	85·2	78·1

TABLE 5.

	Expt. No. 15	No. 16
Wt. of AZDN (mg.)	31·2	25·0
Vol. of styrene (ml.)	6·42	6·90
AZDN decomposed (%), calc.	15·3	5·7
Wt. of TMSDN (mg.) found	0·39	0·18
Wt. of IBN (mg.) found	0·46	0·18
AZDN equiv. of TMSDN (mg.)	0·47	0·22
AZDN equiv. of IBN (mg.)	1·09	0·43
% wasted radicals combining	30·1	33·8

TABLE 6.

	Expt. No. 17	No. 18
Wt. of AZDN (mg.)	277·3	7·75
Vol. of toluene (ml.)	1·4	2·0
Time of reflux (hr.)	3·20	3·67
Wt. of TMSDN (mg.) found	186·8	4·81
Wt. of IBN (mg.) found	8·77	0·20
AZDN equiv. of TMSDN (mg.)	225·3	5·80
AZDN equiv. of IBN (mg.)	20·8	0·47
% radicals combining	91·5	92·5

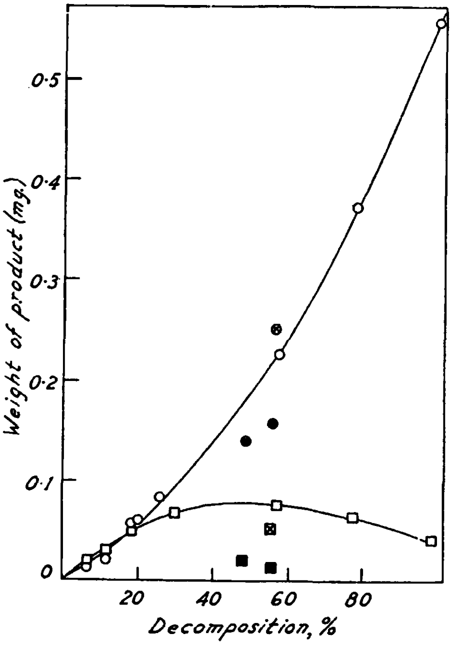
Experiments at 110°.—Solutions of labelled αα′-azo*iso*butyronitrile in toluene were refluxed in air for about 3½ hr., by which time decomposition of the azo-compound was almost complete. The conditions for these experiments approximate to those in Bickel and Waters's experiments (*loc. cit.*). Results are summarized in Table 6.

DISCUSSION

The *iso*butyronitrile produced in the decomposition of αα′-azo*iso*butyronitrile in solvents containing hydrogen could arise either from the disproportionation of pairs of CN•CMe$_2$• radicals or from a reaction in which a radical abstracted a hydrogen atom from a molecule of the solvent. The fact that the quantity of *iso*butyronitrile produced during decomposition in carbon tetrachloride is very similar to the quantities produced in similar experiments in benzene and toluene shows that the hydrogen-abstraction process is of little significance. There is clear evidence that transfer to αα′-azo*iso*butyronitrile is of negligible importance in polymerization reactions (see Bevington, Melville, and Taylor, *loc. cit.*), so it is unlikely that CN•CMe$_2$• radicals would abstract hydrogen atoms from the azo-compound at an appreciable rate. In all experiments in benzene, toluene, and carbon tetrachloride, the weight of αα′-azo*iso*butyronitrile decomposed, calculated from Bawn and Mellish's data (*loc. cit.*), was a little greater than the weight calculated from the weights of tetramethylsuccinodinitrile and *iso*butyronitrile. This difference may be due in part to the chosen velocity constant's being slightly wrong and in part to the fact that some of the radicals disappear by reaction with the methacrylonitrile produced during the decomposition; Bickel and Waters (*loc. cit.*) found evidence that this reaction actually occurs.

Expts. No. 17 and 18 confirm that in toluene at about 110° the major product from the decomposition of αα′-azo*iso*butyronitrile is the combined product. On the other hand, the experiments reported in Table 2 show that at small extents of decomposition at 60° disproportionation of the radicals occurs more frequently than combination. The conditions under which the experiments of Table 2 were performed differ in a number of respects from those prevailing in Expts. No. 17 and 18; Table 3 shows that the differences in results can be ascribed to differences in the extent of decomposition. At 60°, as decomposition proceeds, combination appears to become increasingly important.

The variation in the relative quantities of tetramethylsuccinodinitrile and *iso*butyronitrile during decomposition might be explained by supposing that ordinarily $\alpha\alpha'$-azo*iso*butyronitrile contains two types of molecule the less stable of which gives radicals which tend to undergo disproportionation; the more stable and more abundant form would be assumed to give radicals prone to undergo combination. If this were the case the observation that the two modes of inter-radical reaction vary in importance with the extent of decomposition could be explained qualitatively. This hypothesis is at variance with the fact that it is generally agreed that the decomposition of $\alpha\alpha'$-azo*iso*butyronitrile has no obvious anomalies in the rate–time relationships. In addition, closer examination shows that this hypothesis does not fit the experimental results.



The weights of tetramethylsuccinodinitrile and iso*butyronitrile formed at various stages in the decomposition of* 1 *mg. of* $\alpha\alpha'$*-azo*iso*butyronitrile.*

○ and □ refer to tetramethylsuccinodinitrile and *iso*butyronitrile respectively for experiments in benzene and toluene; ● and ■ to these substances for experiments in the presence of *iso*butyronitrile; ⊗ and ⊠ to these substances for an experiment performed in the presence of tetramethylsuccinodinitrile.

From the results in Tables 2 and 3, the weights of products formed at various stages in the decomposition of 1 mg. of the azo-compound can be calculated. From Fig. 1 it is seen that the weight of *iso*butyronitrile rises to a maximum and then falls off; also the weight of tetramethylsuccinodinitrile is not a linear function of the extent of decomposition. If the hypothesis already discussed were true, the amount of *iso*butyronitrile should increase during the early stages of the reaction but subsequently it should increase only very slowly or remain stationary.

The variations in the relative proportions of tetramethylsuccinodinitrile and *iso*butyronitrile with the extent of decomposition of the azo-compound and the disappearance of *iso*butyronitrile in the later stages of the decomposition could be explained if *iso*butyronitrile and methacrylonitrile, the two products of disproportionation, could interact to form tetramethylsuccinodinitrile fairly slowly at 60°. If this were the case, the amount of *iso*butyronitrile found in the reaction mixture would rise to a maximum and then would gradually decrease as it reacted with methacrylonitrile; also the weight of tetramethylsuccinodinitrile would not be a linear function of the extent of decomposition. By this hypothesis, the actual tendencies of the radicals for disproportionation and combination should be measured by the relative yields of the two types of products in the early stages of the decomposition; by this criterion about 30% of the inter-radical reactions occur by combination.

Consider the results at 50% decomposition; by extrapolation of the results obtained at small extents of decomposition the expected weights of tetramethylsuccinodinitrile and *iso*butyrontrile are 0·100 and 0·126 mg. respectively. The found weights of these products are 0·190 and 0·079 mg. If the *iso*butyronitrile which appears to have been lost reacted with methacrylonitrile to give tetramethylsuccinodinitrile, 0·095 mg. of the latter would be produced. This corresponds closely with the difference between the found and expected weights of the dinitrile. The differences between the calculated and observed weights of tetramethylsuccinodinitrile and *iso*butyronitrile can be correlated similarly at other stages in the decomposition.

It must be supposed that the postulated reaction of *iso*butyronitrile and methacrylonitrile to give tetramethylsuccinodinitrile occurs only in the presence of αα'-azo*iso*butyronitrile, because only a trace of the dinitrile was found after a mixture of *iso*butyronitrile and methacrylonitrile had been kept at 60° for several days. This probably means that the reaction is promoted by $CN{\cdot}CMe_2{\cdot}$ radicals. The following sequence of reactions can be used to explain these results:

$$\text{(i)}\quad CN{\cdot}CMe_2{\cdot} + CH_3{\cdot}C(CN){:}CH_2 \longrightarrow CN{\cdot}CMe_2{\cdot}CMe(CN){\cdot}CH_2{\cdot}$$

$$\text{(ii)}\quad CN{\cdot}CMe_2{\cdot}CMe(CN){\cdot}CH_2{\cdot} + CHMe_2{\cdot}CN \longrightarrow CN{\cdot}CMe_2{\cdot}CMe_2{\cdot}CN + CN{\cdot}CMe_2{\cdot}$$

These reactions add up to

$$CH_3{\cdot}C(CN){:}CH_2 + CHMe_2{\cdot}CN \longrightarrow CN{\cdot}CMe_2{\cdot}CMe_2{\cdot}CN$$

Bickel and Waters (*loc. cit.*) found evidence that radicals attacked methacrylonitrile but wrote the structure of the radical produced as $(CH_3)_2C(CN){\cdot}CH_2{\cdot}C(CN)(CH_3){\cdot}$. This structure would normally be taken as more likely than the one written in equation (i). Other reactions in which the radical produced in (i) might engage are: (iii) Combination with the radical $CN{\cdot}CMe_2{\cdot}$ to give $CN{\cdot}CMe_2{\cdot}CMe(CN){\cdot}CH_2{\cdot}CMe_2{\cdot}CN$; this product was detected by Bickel and Waters (*loc. cit.*). (iv) Disproportionation with the radical $CN{\cdot}CMe_2{\cdot}$ to give $CN{\cdot}CMe_2{\cdot}CMe_2{\cdot}CN + CN{\cdot}CMe{:}CH_2$. (v) Combination with another of its kind; the structure of the radical does not permit of disproportionation in the interaction. This reaction would probably not be of very great importance because the concentration of these radicals would presumably be very low.

On this suggested reaction scheme, it is possible to predict the effect of *iso*butyronitrile upon the apparent production of tetramethylsuccinodinitrile during the decomposition of αα'-azo*iso*butyronitrile. If the $CN{\cdot}CMe_2{\cdot}$ radical in (i) is derived directly from the labelled initiator, it has a high specific activity; it is converted, however, into a radical having very low specific activity because the *iso*butyronitrile engaged in reaction (ii) is composed of a very small weight of material of high activity mixed with a much larger weight of inactive carrier. Some of the radicals of low specific activity combine to give tetramethylsuccinodinitrile of low activity; an error is introduced into the analysis for this substance because it is assumed that all the dinitrile present before the addition of carrier has a high specific activity. The Figure shows that the amount of tetramethylsuccinodinitrile found by analysis in these circumstances is definitely lower than the amount formed in benzene solutions. No satisfactory explanations can be advanced for the very marked reductions in the amounts of *iso*butyronitrile found when the decompositions were performed in the presence of inactive tetramethylsuccinodinitrile or *iso*butyronitrile.

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